

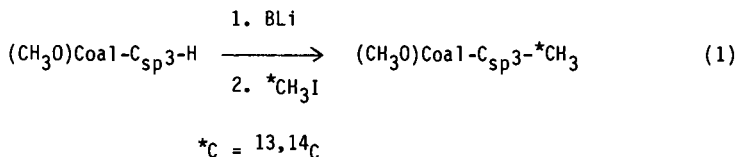
THE IMPORTANCE OF DIPHENYLMETHANE-LIKE STRUCTURAL UNITS IN AN ARGONNE PREMIUM COAL SAMPLE*

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INTRODUCTION

The development and application of chemical and spectroscopic techniques for the purpose of evaluating the acidic O-H and C-H sites in coal has received much attention recently (1-8). In general, these studies have relied on the ability of bases to abstract acidic protons from O-H and C-H sites to generate coal anions. These anions can then be alkylated with a variety of reagents which includes alkyl halides (2,5), alkyl tosylates (4) and alkyl sulfates (6,8). The resultant coal derivatives can be studied by using a combination of chemical and spectroscopic probes such as soxhlet extractability (2,5), pyrolytic behavior (9) and ^{13}C NMR (2,6,7,8).

Our approach (3,6,8) for characterizing the acidic C-H bonds in coal is to treat O-methyl coal with a series of indicator bases, BLi, followed by methylation with C-13,14 double labelled methyl iodide, equation (1).



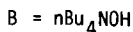
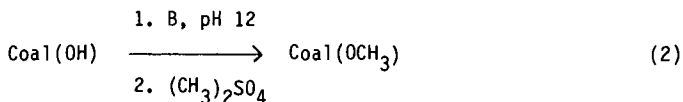
By varying the identity of BLi, and thus the pK_a of the conjugate acid BH, it is possible to evaluate the number of C-H bonds as a function of pK_a . The bases we have used thus far, 9-phenylfluorenyllithium (pK_a , 18.5 (10)), fluorenyllithium (pK_a , 22 (10)) and trityllithium (pK_a , 31 (10)), have allowed us to evaluate the distribution of acidic C-H sites within the three pK_a ranges: $12 < \text{pK}_a < 18.5$, $18.5 < \text{pK}_a < 22$, and $22 < \text{pK}_a < 31$. The application of this approach to two bituminous coals, namely Illinois No. 6 hvCb and PSOC 1197 lvb, led to the discovery of a significant concentration of acidic C-H sites with $18.5 < \text{pK}_a < 22$ which was interpreted as evidence for fluorene-like structural units in coal (6,8).

This approach to coal structure analysis is limited to the evaluation of acidic C-H sites with $\text{pK}_a < 31$. Furthermore, it was shown that PhCH_2Ph (pK_a , 33(11)), the prototypical diarylmethane, is not alkylated to a significant extent upon treatment with trityllithium and methyl iodide (12). For these reasons, we have developed approaches for the evaluation of acidic C-H sites with $31 < \text{pK}_a < 33$. In this article, we illustrate these approaches using Upper Freeport mvb (APCS number 1) as the coal.

*Research sponsored by the Division of Chemical Sciences/Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

RESULTS AND DISCUSSION

The Upper Freeport coal, empirical formula $C_{100}H_{76}S_1O_3$, was O-methylated at pH 12 by using tetrabutylammonium hydroxide as base and natural abundance dimethyl sulfate as previously reported (8), equation (2).



Parallel experiments in which ^{14}C -dimethyl sulfate was employed as the methylating agent established that no more than 0.4 O-methyl groups per 100 coal carbons are formed under these conditions.

The first approach to evaluate the C-H sites with $31 < pK_a < 33$ relies on a comparison of the relative reactivity of the O-methyl coal towards alkylation with base and $^{13,14}\text{CH}_3\text{I}$, where the pK_a of the conjugate acid of the base equals 31 or 33. This was done using trityllithium (pK_a , 31 (10)) and diphenylmethyl-lithium (pK_a , 33 (11)) as the bases. Carbon-14 combustion analysis (13) was used to evaluate the number of methyls introduced with the two bases as a function of the number of repetitive treatments with base and methyl iodide. The data, as shown in Table 1, demonstrate the requirement for a minimum of three multiple treatments to achieve exhaustive methylation. This result parallels our earlier observations on the C-alkylation of O-methyl Illinois No. 6 (3) and O-methyl PSOC 1197 (6,8). This chemical property can be interpreted as evidence for the methylation of structural units which contain multiple acidic C-H bonds such as the methylene group, $-\text{CH}_2-$. The calculation of the number of acidic C-H bonds with $31 < pK_a < 33$ is done by making the difference: number of methyls added with diphenylmethyl-lithium minus number of methyls added with triphenylmethyl-lithium. For O-methyl Upper Freeport, this calculation yields $0.5 \pm 0.2/100$ coal C when the first treatment values are used and $1.1 \pm 0.3/100$ coal C after three treatments.

A second approach was also used to evaluate the number of C-H sites with $31 < pK_a < 33$. This involves the exhaustive methylation of all acidic C-H sites with $pK_a < 31$ followed by methylation using diphenylmethyl-lithium and $^{13,14}\text{CH}_3\text{I}$. Alkylation of the acidic sites with $pK_a < 31$ was accomplished by treating O-methyl Upper Freeport with trityllithium and natural abundance methyl iodide a total of six repetitive treatments. Subsequent methylation of this coal derivative with diphenylmethyl-lithium and $^{13,14}\text{CH}_3\text{I}$ followed by ^{14}C combustion analysis yielded a value of 0.9 C-H sites/100 coal C (1 treatment only). Further work is in progress to determine whether this value increases as a result of multiple treatments.

These preliminary data from the two complementary approaches indicate that diarylmethylene units, ArCH_2Ar , and substituted analogs such as ArC(H)RAR which have C-H sites with $31 < pK_a < 33$ are important structural entities in the Upper Freeport coal. Considering only the first treatment data from each approach

where multiple alkylation at $-CH_2-$ groups is assumed to be negligible, then the number of these structural types can be estimated as 0.5 - 0.9 per 100 coal carbons.

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Table 1. C-Methylation of O-Methyl Upper Freeport by using BLi and $^{13,14}\text{CH}_3\text{I}$ in THF at 0°C

Base, BLi (pK_a , BH)	Treatment No.	No. $^{14}\text{CH}_3/100$ Coal C
trityllithium (31)	1	0.61 ± 0.06
	2	0.90 ± 0.09
	3	1.1 ± 0.1
diphenylmethyllithium (33)	1	1.1 ± 0.1
	2	1.8 ± 0.2
	3	2.2 ± 0.2